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TRANSLATION

TRANSACTIONS OF SYMPOSIUM ON HEAT-RESISTANT
MATERIALS (SELECTED ARTICLES)

FOREIGN TECHNOLOGY DIVISION

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UNEDITED ROUGH DRAFT TRANSLATION

TRANSACTIONS OF THE ACADEMY OF SCIENCES OF THE
UKRAINIAN SSR. INSTITUTE OF METAL CERAMICS
AND SPECIAL ALLOYS. SEMINAR ON HEAT-RESISTANT
MATERIALS. (SELECTED ARTICLES)

English Pages: 46

SOURCE: Russian Book, Trudy Akademiya Nauk
Ukrayinskoyi RSR. Institut Metallokeramiki
I Spetsialnykh Splavov. Seminar Po Zharostoykim
Materialam, Nr. 6, Kiev, 1961, pp. 38-58,
64-74.

S/700-61-0-6

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CHEMICAL PROPERTIES AND METHODS OF ANALYZING

CHROMIUM CARBIDES

by: T. Ya. Kosolanoba and G. I. Samsonov

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The chromium carbides, particularly Cr_3C_2 , exhibit low specific gravity, high hardness, wear resistance and scale resistance /1-4/. On this account alloys with a chromium carbide base are commonly used in a number of industries for making parts operating at high temperatures.

There are few data available on the behavior of chromium carbides in different chemical media /4-6/. In view of this, we made a study of the solubility of chromium carbide specimens in the powder and compacted form in a variety of acidic and alkaline media, and of their resistance to oxidation.

The carbides Cr_3C_2 and Cr_7C_3 were prepared by methods described in detail in /7-8/ and Cr_{23}C_6 was made by hot pressing a mixture of chromium and carbon with a calculated composition at 1400° for 30 minutes at 160 kg/cm² in an argon atmosphere. The chemical composition of the carbides used is shown in Table 1.

Table 1
Chemical composition of carbides used.

Carbide	Theoretical composition, %		Composition of carbides used, %		
	Cr	C	Cr	Cbond	Cfree
Cr_3C_2	86.67	13.33	86.36	13.39	0.22
Cr_7C_3	90.99	9.01	90.78	8.88	0.22
Cr_{23}C_6	94.32	5.68	91.03	5.80	0.05

Stability in acidic and alkaline media

The study of chromium carbide powders in different media was made both at room temperature and during heating. The size of the powder particles was 5 microns. The stability of the compacted specimens was studied during heating.

To study the stability of carbides at room temperature, 0.2 g carbide powder was treated with 50 ml solvent and kept for 48 hours at room temperature. The undissolved residue was filtered off, dried and weighed, and the chromium content ~~then~~ in the solution was determined. The experimental results obtained show the high stability of the carbides Cr_3C_2 and Cr_7C_3 and the lower stability of the carbide Cr_{23}C_6 .

Treatment by acids, ~~including mixtures~~ ^{of them,} and solutions of alkali at elevated temperatures was carried out by heating portions of the carbides (0.5 g) in a flask with a reflux condenser. The undissolved residue was filtered off and weighed. The amount of chromium in the solution was determined and the results are shown in Tables 2, 3 and 4. Table 3 gives the results of study of the behavior of the carbides Cr_3C_2 and Cr_7C_3 in organic acids.

Table 2

Behavior of chromium carbides in mineral acids and mixtures of them, (heating time one hour).

Medium	Temperature, °C	Undissolved residue, %	Cr content in solution, %	Temperature, °C	Undissolved residue, %	Cr content in solution, %	Temperature, °C	Undissolved residue, %	Cr content in solution, %
Sulphuric acid (1.84)	280	—	58.4	265	—	89.7	—	—	—
Sulphuric acid (1:1)	136	6.51	27.8	137	1.62	87.9	135	1.3	88.9
Sulphuric acid (1:10)	105	95.3	4.5	100	13.6	78.6	107	4.3	86.1
Sulphuric and nitric acid	120	83.5	14.1	125	90.6	8.2	127	96.7	1.3
Hydrochloric acid (1:1)	108	96.2	2.90	110	3.49	85.9	110	3.9	86.6
Hydrochloric and nitric acids (3:1)	106	90.9	7.40	106	93.8	5.07	104	97.5	1.3
Hydrochloric acid and hydrogen peroxide	—	—	—	105	5.6	85.0	100	99.0	traces
Phosphoric acid	—	—	—	112	95.5	4.2	—	—	—
CrO_3 in sulphuric acid	120	33.2	—	100	53.2	—	—	—	—

It follows from Table 2 that Cr_3C_2 is the most stable carbide and Cr_{23}C_6 is the least stable. The addition of oxidizers to acids inhibits the dissolution of the carbides through the formation of a passivating chromium-oxide film. Pronoun-

ced passivation is observed in the most chromium-rich carbide Cr_{23}C_6 , which for practical purposes does not dissolve in mineral acids in the presence of oxidizers.

Table 3
Behavior of chromium carbides in organic acids (heating time one hour).

Medium	Temperature, °C	Undissolved residue, %	Cr content in solution, %	Temperature, °C	Undissolved residue, %	Cr content in solution, %
Tartanic acid (50%)	100	99.9	Not detected	102	99.7	Not detected
Citric acid (saturated solution)	100	100.0	Ditto	108	99.4	Ditto
Formic acid (concentrated)	118	99.3	Ditto	120	98.8	Ditto
Acetic acid	115	98.8	0.31	112	98.9	0.42
Oxalic acid (saturated solution)	100	98.5	1.21	104	95.5	3.99

Table 4
Behavior of chromium carbides in alkaline solutions (heating time one hour).

Medium	Temperature, °C	Undissolved residue, %	Cr content in solution, %	Temperature, °C	Undissolved residue, %	Cr content in solution, %	Temperature, °C	Undissolved residue, %	Cr content in solution, %
NaOH, 30 solution	110	95.5	4.32	110	96.3	3.54	104	95.6	1.4
NaOH and bromide water,	110	99.8	same	110	96.1	4.01	—	—	—
Alkaline solution	106	88.1	7.6	102	85.9	9.7	104	85.0	11.3
$\text{K}_3[\text{Fe}(\text{CN})_6]$	100	61.5	—	100	53.2	—	—	—	—

For our study of the behavior of compacted carbide specimens 8 mm in diameter and 10 mm high, the compacts were heated in the appropriate solutions in flasks with reflux condensers ; the chromium content in the solution was determined (Table 5).

The data contained in Table 5 show the higher stability of compacted carbide specimens, compared with those in the powder form. The stability of Cr_{23}C_6 is less than for Cr_7C_3 and Cr_3C_2 . In mineral acids the stability of Cr_{23}C_6 is sharply increased by the presence of oxidizers.

The chemical stability of chromium carbides is related to their crystal

Table 5

Behavior of compacted chromium carbide specimens in different media (one hour).

Medium	Temperature, °C	Cr content in solution, %	Corrosion rate, g/m ² hr.	Temperature, °C	Cr content in solution, %	Corrosion rate, g/m ² hr.	Temperature, °C	Cr content in solution, %	Corrosion rate, g/m ² hr.
Sulphuric acid (1:1)	136	traces	0.003	125	21.2	26.4	120	29.0	70.1
Sulphuric acid (1:1)	112	0.21	0.039	110	4.7	7.5	110	19.2	44.5
Nitric acid (1:1)	112	Not detected	—	112	0.00	—	115	Not detected	—
Hydrochloric and nitric acids (3:1)	102	0.33	0.15	108	0.06	0.036	110	Same	0
Sulphuric and nitric acids	124	—	0.052	130	0.18	0.14	128	Same	0
Phosphoric and sulphuric acids	184	Not detected	—	185	0.41	—	170	22	61.6
Oxalic acid	130	Same	0.015	135	Not detected	0.036	132	Not detected	0
Caustic soda and bromine water	110	0.29	0.12	115	0.36	—	112	0.43	0.7

structure, particularly to the configuration of the carbon atoms in the elementary cells. Least stable is the carbide Cr_{23}C_6 , which exhibits a characteristic isolation of the carbon atoms; the carbides Cr_3C_2 and Cr_7C_3 are much more stable and in their structure the carbon atoms form chains, Cr_3C_2 being more stable and having a rhombic cell with zig-zag chains of carbon atoms similar to the FeB cell [1]. This observation is in close agreement with the data obtained by Markovskiy and Kondrashov [9], which show that the chemical stability of the borides of transition metals is increased as the structural elements made of boron atoms grow more complex.

For our study of the oxidation resistance of the chromium carbide powders, portions weighing 0.5 g were burned in a muffle furnace in an oxygen stream at temperatures ranging from 400 to 1000° (at intervals of 100°). The amount of oxidized carbon was determined by the absorption-volumetric method and characterized the degree of oxidation. In order to obtain comparable results in calculating the amount of carbon burned up, the overall initial content in each carbide was taken as 100%.

The results, shown in Table 6, indicate that the oxidation of the carbides proper begins at 700°, and it is only the free carbon which is oxidized at lower

temperatures.

Processing of the data obtained for oxidation of Cr_3C_2 between 800 and 1000°, and the logarithmic graph plotted to show the oxidation rate as a function of time, indicate that the oxidation follows a parabolic law and can be expressed by the equations

$$y_{800}^{1.9} = 1.091\tau;$$

$$y_{900}^{2.56} = 36.44\tau;$$

$$y_{1000}^{2.1} = 50.23\tau.$$

The oxidation of the carbide Cr_7C_3 obeys a more complex logarithmic law and is expressed by the equations

$$y_{800} = 97 \lg \tau + 4;$$

$$y_{900} = 196 \lg \tau + 156;$$

$$y_{1000} = 100 \lg \tau + 672.$$

where y is the degree of oxidation in terms of the amount of oxidized carbon, %;

τ is the oxidation time in minutes.

The oxidation isotherm for the carbide with the lowest carbon content at 800° is expressed by a parabolic equation

$$y_{800}^{1.44} = 28.4\tau,$$

and at 900 and 1000° by logarithmic equations

$$y_{900} = 100 \lg \tau + 98;$$

$$y_{1000} = 98 \lg \tau + 165.$$

Hence the nature of the oxidation varies with the carbide.

The compacted specimens were oxidized by continuous weighing at temperatures between 800 and 1000°. According to the data given in Table 7, compacted specimens of the carbide Cr_3C_2 and Cr_{23}C_6 do not oxidize at all for practical purposes at temperatures up to 1000°. Cr_7C_3 is less stable and already oxidizes appreciably at 800°, following a logarithmic law expressed by the equations

Amount of burned carbon as function of temperature, % (overall initial content of carbon in carbides taken as 100%).

Amount of Burned Carbon as function of temperature; 20°C/min. and constant																		
Tempera- ture, °C	Time, min.																	
	10			20			30			40			50			60		
	Cr ₃ C ₂	Cr ₇ C ₃	Cr ₁₃ C ₆	Cr ₃ C ₂	Cr ₇ C ₃	Cr ₁₃ C ₆	Cr ₃ C ₂	Cr ₇ C ₃	Cr ₁₃ C ₆	Cr ₃ C ₂	Cr ₇ C ₃	Cr ₁₃ C ₆	Cr ₃ C ₂	Cr ₇ C ₃	Cr ₁₃ C ₆	Cr ₃ C ₂	Cr ₇ C ₃	Cr ₁₃ C ₆
400	0.1	0.23	0	0.24	0.67	0	0.32	0.67	0	0.39	0.67	0	0.39	0.67	0	0.39	0.67	0
500	0.89	1.55	0.5	1.04	1.66	0.5	1.04	1.66	0.5	1.04	1.66	0.5	1.04	1.66	0.5	1.04	1.66	0.5
600	0.97	1.99	0.8	1.34	2.66	0.8	1.49	2.88	0.8	1.64	2.88	0.8	1.64	2.88	0.8	1.64	2.88	0.8
700	2.68	3.54	1.71	4.38	4.76	3.08	4.98	5.42	3.77	5.20	5.86	4.11	5.42	6.19	4.62	5.64	6.75	4.96
800	2.53	10.06	7.7	5.12	13.60	10.77	6.76	15.03	12.48	7.87	16.03	14.88	8.62	16.80	16.59	9.58	17.46	18.64
900	9.95	22.66	20.00	14.10	41.55	22.80	15.20	44.87	24.11	16.72	45.86	25.48	18.19	48.00	26.84	19.31	51.83	28.21
1000	14.26	72.05	28.55	25.91	81.44	32.12	32.30	83.54	33.85	37.87	84.20	35.56	40.84	84.71	36.59	43.58	84.87	38.29

Results of experiments on oxidizing chromium carbides with soot additives (temperature 600°)¹.

Temperature, °C	Time, min.															
	Cr ₃ C ₂						Cr ₇ C ₃						Cr ₂₃ C ₆			
	30	60	90	120	30	60	90	120	150	180	210	240				
800	0	0	0	0	0.0059	0.0007	0.0105	0.0121	0.0128	0.0128	0.0129	0.0128	0	0	0	0
900	0	0	0	0	0.0165	0.0287	0.0327	0.0354	0.0391	0.0421	0.0443	0.0470	0	0	0	0
1000	0	0	0	0	0.0130	0.0420	0.0621	0.0899	0.0800	0.0903			0	0	0	0

$$y_{400^{\circ}} = 1,5 \lg \tau - 1,4;$$

$$y_{500^{\circ}} = 3,5 \lg \tau - 3,3;$$

$$y_{1000^{\circ}} = 14 \lg \tau - 17,7.$$

The study of the resistance to oxidation of the chromium carbide powders has made it possible to work out a method of determining the amount of free carbon in them.

The normally used method of determining free carbon in carbides, which is based on dissolving the carbide in a mixture of nitric and hydrofluoric acids, in which the free carbon remained in the form of an insoluble residue, cannot be used in the given case since chromium carbides do not dissolve in this mixture. Treating the carbide with a H_2SO_4 solution of CrO_3 , used by Meyerson and Samsonov, /10/ for determining the free carbon in boron carbide, was not successful, either, on account of ^{only} slight solubility of the carbides in this mixture.

The theoretical method of determining the free carbon used so far is based on treating the carbide with hydrochloric acid, determining the chromium and carbon content in the weighed undissolved residue, which constitutes Cr_3C_2 and free carbon, and then calculating the amount of carbon bonded with the chromium, and the free carbon. The method is not very effective; it is tedious and involves large errors, and when the free carbon content is small (up to 0.5%) it is of no use for practical purposes.

On account of the fact that the oxidation of chromium carbides begins at temperatures above 700° it has been suggested that the free carbon oxidizes at lower temperatures.

To test this hypothesis we burned the carbides Cr_3C_2 and Cr_7C_3 with a measured soot additive at 600° . The results of the experiments, given in Table 8, show that at this temperature the free carbon is fully burned up in 30 or 40 minutes. Relative error in this determination is 5 - 8 %.

The results of parallel calculations of the free carbon content in Cr_3C_2 and Cr_7C_3 show the satisfactory reproducibility and possibility of applying this method to the analysis of chromium carbides.

Conclusions

1. We studied the behavior of chromium carbide specimens in the powder and compacted form at room temperature and when heated in different chemical media.

It was established that in order of descending stability in mineral acids, mixtures of them, and solutions of alkalies, the carbides can be arranged in the series Cr_3C_2 - Cr_7C_3 - Cr_{23}C_6 , which is linked with their crystal structure.

The stability of the carbides is increased in the presence of oxidizing agents, and in this case they can be arranged in the sequence Cr_3C_2 - Cr_7C_3 - Cr_{23}C_6 according to the degree of increase in stability.

2. We studied the oxidation resistance of chromium carbide specimens in the powder and compacted form at temperatures up to 1000° in an oxygen stream.

It was found that the oxidation of all the carbide powders begins at 700° .

The laws governing the oxidation vary with the carbides.

Compacted specimens of carbides Cr_3C_2 and Cr_{23}C_6 are not oxidized for practical purposes up to 1100° .

Table 8

Results of experiments on oxidizing chromium carbides with soot additives
(temperature 600°)¹.

							Relative error, %
Cr ₃ C ₂ No. 1 +1.01% C	0.68	1.14	1.21	1.22	1.22	1.22	0.08
Cr ₃ C ₂ No. 1 +1.35% C	0.48	1.26	1.41	1.45	1.45	1.45	7.6
Cr ₃ C ₂ No. 1 +3.98% C	1.59	3.14	3.61	3.80	3.87	3.90	6.2
Cr ₃ C ₂ No. 1 +0.48% C	0.34	0.47	0.47	0.47	0.47	0.47	7.3
Cr ₃ C ₂ No. 1 +1.24% C	0.46	1.22	1.31	1.31	1.31	1.31	3.1
Cr ₃ C ₂ No. 1 +1.61% C	1.10	1.51	1.55	1.55	1.55	1.55	5.5
Cr ₃ C ₂ No. 1 +2.24% C	1.33	2.02	2.11	2.11	2.11	2.11	7.0
Mean deviation							5.3%
Cr ₇ C ₃ +1.12% C	0.54	1.08	1.23	1.26	1.26	1.26	5.8
Cr ₇ C ₃ +1.27% C	0.80	1.31	1.37	1.37	1.37	1.37	8.0
Cr ₇ C ₃ +1.63% C	0.53	0.85	1.54	1.69	1.69	1.69	8.7
Cr ₇ C ₃ +2.46% C	0.76	2.02	2.36	2.43	2.43	2.43	9.3
Cr ₇ C ₃ +3.80% C	2.30	3.66	3.78	3.78	3.78	3.78	5.8
Mean deviation							7.5%

3. A method of determining the amount of free carbon in chromium carbides has been worked out on the basis of our study of their oxidation resistance.

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CHEMICAL PROPERTIES AND METHODS OF ANALYZING BORIDES

OF TRANSITION AND RARE-EARTH METALS

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The borides of transition metals in the fourth, fifth and sixth groups of the periodic table plus the borides of rare-earth elements are commonly used in various branches of engineering on account of their hardness, heat resistance and special electric, magnetic and chemical properties /1, 2/.

Tables 1 and 2 give data on the chemical composition of the borides of transition and rare-earth metals.

Table 1

Chemical composition of borides of transition metals.

Ti-B	Zr-B	Nb-B	Ta-B	V-B	Cr-B	Mo-B	W-B	Ni-B
Ti ₂ B	—	Nb ₂ B	—	—	Cr ₂ B	Mo ₂ B	W ₂ B	Ni ₂ B
TiB	ZrB	NbB	TaB	VB	CrB	MoB	WB	NiB
TiB ₂	ZrB ₂	NbB ₂	TaB ₂	VB ₂	CrB ₂	MoB ₂	WB ₂	Ni ₂ B ₂
Ti ₂ B ₃	—	—	—	—	Cr ₂ B ₂	Mo ₂ B ₂	—	Ni ₂ B ₂
TiB ₁₂	—	—	—	—	—	Mo ₂ B ₅	W ₂ B ₅	—

Our studies were carried out with titanium, zirconium, vanadium, niobium and chromium diborides, with Mo₂B₅ and W₂B₅ and the hexaborides of the rare-earth elements.

We studied the stability of borides in acids. Titanium, zirconium, niobium, tantalum, chromium, vanadium, molybdenum and tungsten borides are stable with respect to hydrochloric acid. When heated with concentrated sulphuric acid, zirconium, niobium, tantalum, molybdenum and vanadium borides decompose, while chromium boride is decomposed by dilute sulphuric acid. Vanadium and chromium boride dis-

solve in perchloric acid. Only chromium boride dissolves completely in hydrochloric acid. We studied the solubility of boride in aqua regia, the mixtures $\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}_2 + \text{HNO}_3$, $\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4$, HCl +bromine water, $\text{HCl} + \text{HClO}_4$, and also in the mixtures $\text{HNO}_3 + \text{HF}$ and $\text{H}_2\text{SO}_4 + \text{HNO}_3$. The least stable is vanadium boride, which partially dissolves in all the acids, and completely in nitric acid. The most stable are the borides of niobium and tantalum, especially tantalum boride, which is not decomposed by mineral acids or acid mixtures.

Practically all the borides mentioned (with the exception of NbB_2 and TaB_2) are completely decomposed by the mixtures $\text{HNO}_3 + \text{HF}$ and $\text{H}_2\text{SO}_4 + \text{HNO}_3$.

Table 2

Chemical composition of borides of rare-earth elements.

MeB_2	MeB_4	MeB_6	MeB_{12}
ScB_2	YB_4	For all rare-earth elements except Tu and Pm	LaB_{12}
YB_2	CeB_4		—
—	PrB_4		—
—	SmB_4		—
—	GdB_4		—
—	DyB_4		—
—	HoB_4		—
—	LuB_4		—

All the borides are easily decomposed by melted alkalis, carbonates and bisulphates of alkaline metals and sodium peroxide.

The hexaborides of the rare-earth elements can be comparatively easily decomposed by acids (Table 3). In dilute nitric acids, all the hexaborides decompose rapidly and completely, even in the cold state, or when slightly warmed. They also decompose easily in a mixture of perhydrol and nitric acid, and in a sulphuric and nitric acid mixture. The hexacarbides are more resistant to the action of hydro-

chloric and sulphuric acids.

Table 3

Solubility of borides of rare-earth elements in acids and acid mixtures.

Boride	HNO ₃ (1:1)	Aqua regia (1:1)	H ₂ SO ₄ (1:1) + 5 drops HNO ₃	In soluble residue, %	
				HCl (1:1) (2 hr)	H ₂ SO ₄ (1:1) (2 hr)
LaB ₆	Dissolves completely when warmed for 5 minutes.	Dissolves completely when warmed for 5 minutes.	Dissolves completely when warmed for 5 minutes.	93-94	89-92
CeB ₆	The Same	The Same	The Same	84-86	83-84
SmB ₆	" "	" "	" "	79-80	77
YB ₆	" "	" "	" "	77-78	71-72
NdB ₆	" "	" "	" "	87-88	78
PrB ₆	" "	" "	" "	90-94	27-30
GdB ₆	" "	" "	" "	91-93	87

All these hexaborides decompose when melted together with caustic alkalis, alkaline metal carbonates and sodium peroxide.

Analysis of borides of transition metals

In the borides of transition metals we determine the overall amount of boron, metal and carbon, and in the case of certain borides the content of free boron.

In determining the total amount of boron, great difficulties are experienced in decomposing the samples. Melting them with soda and using oxidizing agents puts platinum crucibles out of action fairly rapidly. We found that the borides of many metals can be decomposed by melting them with a mixture of alkali and a small amount of sodium peroxide, or with sodium peroxide in iron crucibles.

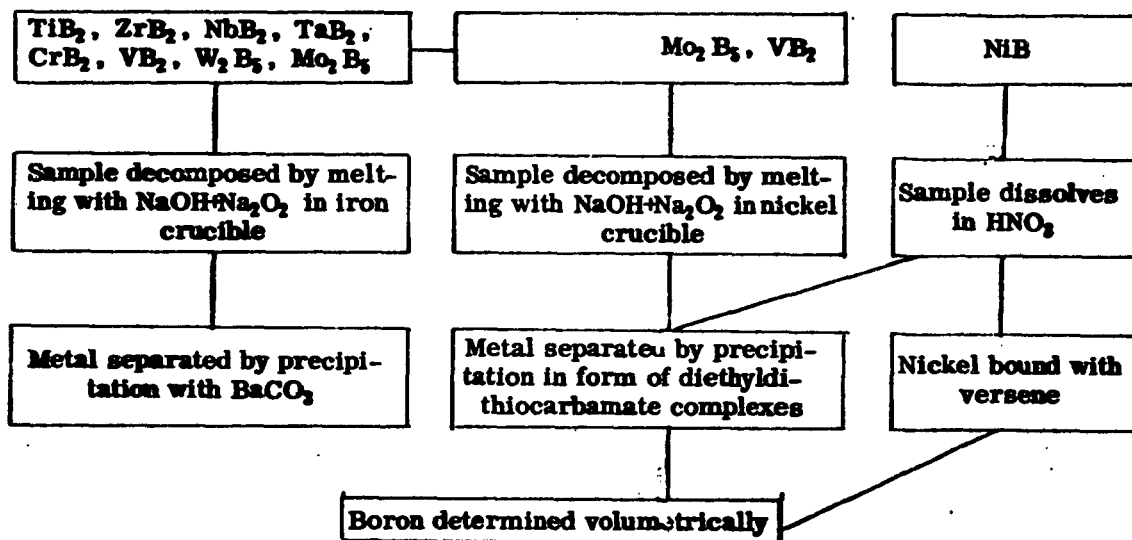
Nickel boride can be dissolved in nitric acid. When the sample has dissolved and the metal has separated, the boron is determined volumetrically. Many metals can be separated from the boron by precipitating them with barium hydroxide, barium carbonate or calcium carbonate.

Verification of methods of separating metals from boron shows that the process occurs most fully when barium carbonate is used for the precipitation, hence we used this substance to separate titanium, zirconium, niobium, tantalum, chromium and tungsten.

Nickel, vanadium and molybdenum were separated from the boron by extraction of their diethyldithiocarbatic complexes with chloroform. Vanadium and molybdenum can also be separated from boron by precipitating them with barium carbonate. When precipitating vanadium, it is essential to have trivalent iron ions in the solution, and when precipitating molybdenum there must be trivalent iron ions or calcium ions in the solution. The boron in nickel boride can be determined without separating the nickel if we bind it with trilon B (table 4).

Table 4

Analysis of borides of transition metals.



As soon as the metals have been precipitated out, the boric acid is trans- formed by means of glycerine, mannitol or invert sugar into a stronger complex acid, which is then titrated with caustic soda in the presence of phenolphthalein. The best results are obtained by using mannitol or invert sugar.

To determine the metals in titanium, zirconium, vanadium and chromium borides, the weighted portions are dissolved in a mixture of H_2SO_4 and HNO_3 . The solution is evaporated until SO_3 is given off and the metal is determined. The

borides of niobium, tantalum and molybdenum are decomposed by melting them with sodium peroxide in a nickel crucible.

Tungsten boride is decomposed in a platinum bowl in a mixture of HF and HNO_3 . Zirconium, niobium and tantalum are determined by the gravimetric method by precipitation with cupferronate, titanium by the gravimetric or volumetric method, and vanadium and chromium by the volumetric method. Molybdenum is precipitated in the form of lead molybdenate. Tungsten is separated in the form of tungstic acid. To determine nickel the method of titrating with versene and the indicator murexide is used.

Analysis of borides of rare-earth elements

In the borides of rare-earth elements we determine the overall amount of boron, rare-earth element and carbon.

Determining rare-earth elements in hexacarbides of yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, ytterbium and in thorium hexaboride.

We used the method of titrating rare-earth elements with a versene solution using the indicator arsenazo /4/. A portion of boride was dissolved in nitric acid. The solution was transferred to a measuring flask. An aliquot part of the solution was removed and placed in a conical flask, 3 to 5 drops of pyridine were added, the solution was diluted with water, neutralized with ammonia until the pH value was 6 or 7, two drops of arsenazo solution were added and the rare-earth element 0.02 M was titrated with a versene solution until the violet tinge turned pink. Thorium was titrated at a pH value from 2 to 4.

Determining boron in the borides of rare-earth elements.

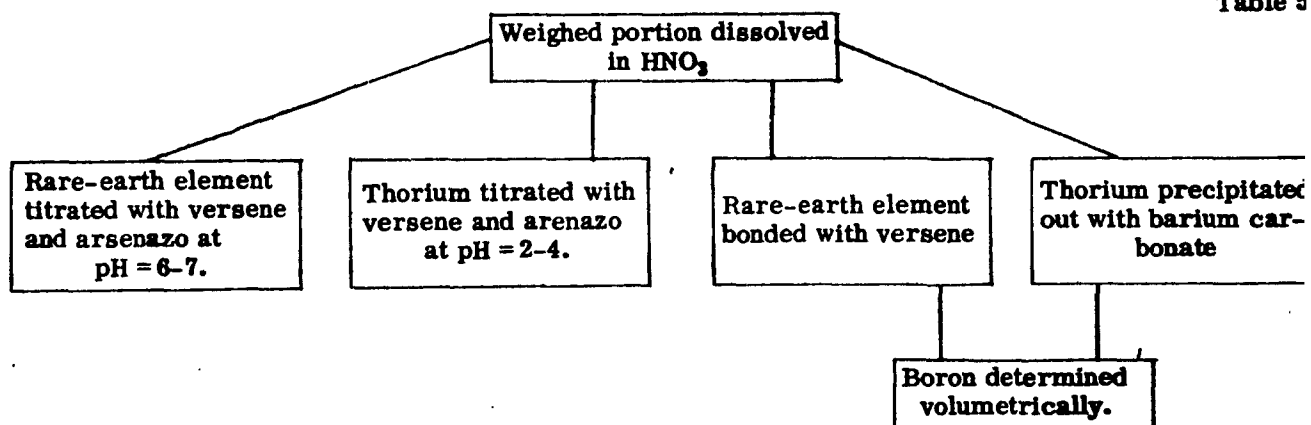
We developed a method of determining boron in the borides of rare-earth elements without precipitating out the latter.

Rare-earth elements can be bound into a complex compound by versene and do not prevent the boron being determined by the volumetric method. The boron is determined in the following way. With a pipette we remove ~~an~~ aliquot part of the solution from the measuring flask (see determination of rare-earth elements) and transfer it to a conical flask, add from a burette ~~the~~ exact number of milliliters of 0.02 n versene solution required to bind the rare-earth element; the solution is then neutralized with caustic soda using methyl red, after which the boron is determined ~~in the~~ ^{way} ~~usual~~ by titration with a 0.1 n caustic solution plus invert sugar and mannitol, using phenolphthalein as the indicator.

At the same time we determine ^{the} boron after precipitating out the rare-earth elements with barium carbonate. Results a little too high were only obtained in the case of samarium hexaboride (0.5 - 1.0%), hence we recommend determining the boron in samarium boride after precipitating out the samarium with barium carbonate. Table 5 shows the analysis of rare-earth element borides in schematic form.

Analysis of hexaborides of rare-earth elements and thorium.

Table 5



Determining free boron in borides of transition and rare-earth

metals

Amorphous boron may be oxidized by a number of agents into boric acid. Among these oxidizing agents are potassium permanganate /5/, quadrivalent cerium sulphate /6/, a mixture of perhydrol and nitric acid /7/ and also potassium iodate and periodate /8/.

At an earlier stage our laboratory developed a method of determining the free boron in boron carbide /9/ based on the different oxidizability of free boron and carbide-bonded boron.

In this paper we studied the ratio of the borides of transition metals TiB_2 , ZrB_2 , CrB_2 , NbB_2 , W_2B_5 and the hexaborides of rare-earth elements YB_6 , LaB_6 , CeB_6 , PrB_6 , NdB_6 , SmB_6 and Gd_2B_6 in the various oxidizing mixtures able to oxidize amorphous boron. As mixtures of this kind, we used perhydrol and nitric acid, sulphuric acid solution of potassium iodate, and a sulphuric acid solution of cerium sulphate.

It was assumed that on the basis of the different degrees of stability of free boron and the enumerated borides with respect to different oxidizing mixtures, it would be possible to develop a method determining the amount of free boron in these borides.

Stability of borides in perhydrol and nitric acid solutions

It has been found by study of the behavior of different borides in a perhydrol-nitric acid mixture that zirconium diboride is the most stable compound with respect to this solvent. The remainder of the borides discussed are either completely decomposed by this mixture (YB_6 , LaB_6 , CeB_6 , PrB_6 , NdB_6 , SmB_6 , Gd_2B_6) or else partially (CrB_2 , TiB_2 , W_2B_5), hence oxidation by a perhydrol and nitric acid mixture was only studied for the case of zirconium diboride. The time over which the specimens were treated with $H_2O_2 + HNO_3$ ranged between 30 and 60 minutes. A perhydrol mixture (1:2 and 1:3) with 10 drops of nitric acid was used for the dissolving. Exactly the same amount of boron goes into the solution, no matter for how long the diboride is treated or how concentrated the perhydrol (Table 6).

The residue obtained after the first treatment with the perhydrol-nitric acid solution was treated for a second time with the same mixture for the same amount

of time. During the second treatment of the zirconium diboride with the oxidizing mixture the boron did not transfer to the solution.

In order to test the suggested method we carried out a number of determinations of the free boron in artificial mixtures of ZrB_2 +amorphous boron (Table 7).

Table 6
Dissolution of ZrB_2 in mixture of perhydrol and nitric acid.

No. of specimen	Mixture of 20 ml perhydrol (1:3) plus 10 drops nitric acid			Mixture of 20 ml perhydrol (1:2) plus 10 drops of nitric acid		
	Portion, g	Treatment time, min	(%) free boron	Portion, g	Treatment time, min	(%) free boron
1	1.0	10	0.09	1.0	10	0.085
	1.0	10	0.087	1.0	10	0.085
	1.0	10	0.085	1.0	10	0.090
	0.5	0	0.085	1.0		
	0.5	5	0.09	1.0		
2	1.0	30	None	1.0	30	None
	1.0	45		1.0	45	
	1.0	60		1.0	60	
	0.5	30				

Table 7
Determining free boron in artificial mixtures of ZrB_2 +amorphous boron (dissolved in mixture of perhydrol (1:3) plus 10 drops HNO_3)

Portion, g	Free boron content, %	Boron added, mg	Boron obtained, mg	Relative error, %
0.5	—	8.3	8.5	+0.24
0.5	—	14.9	15.0	+0.2
0.5	—	20.6	20.3	-1.5
0.5	—	23.1	22.8	-1.25
0.5	—	30.3	29.9	-1.41
0.5	—	43.0	42.5	-1.25
0.5	—	49.0	48.9	-0.2
0.5	—	51.0	50.8	-0.5

Consequently, the free boron in zirconium diboride can be determined with fair accuracy by the following method. 1 g of ZrB_2 is dissolved in a mixture of 20 ml perhydrol with 10 drops of nitric acid for 30 or 40 minutes. The residue is filtered off, the filtrate is neutralized with caustic soda, using methyl red as the indicator, and the boron is then determined as usual by titration with a 0.1 n or 0.01 n caustic soda solution.

Stability of borides in acid solutions of potassium iodate and cerium sulphate

According to published data [6], the diborides of chromium, titanium and zirconium, as well as boron nitride and carbide do not dissolve, either in the cold

or when heated, in acid solutions of potassium iodate and periodate. At the same time data is cited to the effect that elementary boron can be fairly easily turned into a solution when acted upon by these oxidizing agents.

We attempted to use sulphuric acid solutions of potassium iodate and periodate as reagents for determining the free boron in chromium, titanium and zirconium borides, and, if it proved possible, in the hexaborides of the rare-earth elements.

Our experiments showed that titanium, zirconium and chromium borides are partially decomposed by a sulphuric acid solution of potassium iodate. The hexaborides of the rare-earth elements are totally decomposed by a sulphuric acid solution of potassium iodate when slightly warmed.

Similarly, all the borides studied are unstable in acid solutions of cerium sulphate.

Thus, acid solutions of cerium sulphate and potassium iodate cannot be used to determine the free boron in borides.

Conclusions

1. We developed a method of determining boron in the borides of titanium, zirconium, niobium, tantalum, chromium, tungsten, molybdenum, nickel and vanadium. Nickel boride is decomposed by nitric acid, while the other borides are decomposed by melting them with alkalies in iron or nickel crucibles.

To separate titanium, zirconium, niobium, tantalum, chromium or tungsten from boron, we can use barium carbonate, and to separate nickel, molybdenum and vanadium from boron, we extract their diethyldithiocarbamate complexes with chloroform.

To separate molybdenum and vanadium from boron we can precipitate with barium carbonate in the presence of Ca^{2-} or Fe^{3+} ions (for molybdenum) and in the presence of Fe^{3+} ions (for vanadium).

As soon as the metals have been separated from the boron, the latter can be determined alkalimetrically in the presence of invert sugar.

2. A rational method is given for analyzing the borides of rare-earth metals. A weighed portion of boride is dissolved in nitric acid. The rare-earth element and the boron are determined from the aliquot parts: the rare-earth elements by titration with versene with the indicator arsenazo, and boron is determined alkalimetrically after being bound into a rare-earth element complex with an exact amount of versene.

3. We have developed a method of determining free carbon in zirconium diboride based on the different degrees of oxidizability of free boron and boron bound by a mixture of perhydrol and nitric acid.

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ANALYSIS OF TITANIUM, CHROMIUM AND ZIRCONIUM BORIDES

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Dissolution

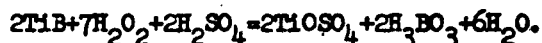
The borides of transition metals constitute a class of compounds somewhere between the intermetallic and interstitial phases /1/. They are very close to the carbides in chemical properties. A characteristic feature of both is high resistance to the action of acids both in the cold state as well as when heated.

Borides can easily be decomposed by fused alkalis, bisulphates and carbonates of alkaline metals. This property is utilized in analytical practice to decompose the borides.

But the melting of them together with caustic soda and sodium peroxide in nickel and iron crucibles gives rise to a number of practical difficulties and hardly meets the requirements of mass analysis.

The aim of our research was to find a simpler method of decomposing the borides and then determining their components.

We found that the borides and biborides of chromium, titanium and zirconium are quantitatively decomposed by sulphuric acid in the presence of perhydrol. The reaction is evidently as follows:



Our experiments show that for complete dissolution of titanium and zirconium borides in a mixture of sulphuric acid and perhydrol we need only heat them until SO_3 is generated; chromium borides have to be dissolved for another 3 to 5 minutes after the SO_3 vapor is given off and the chromium ions acquire a color (+3).

At the same time we verified the volatility of boron when borides are dissolved in a flask with a reflux condenser and also without one. The boron content was determined by the volumetric method - by titration of the solution with alkali in

the presence of phenolphthalein and mannitol. The experiments showed that in the presence of hydrogen peroxide no boron is lost through evaporation.

In this way, the borides can be dissolved in a mixture of sulphuric acid and hydrogen peroxide in an open flask provided the heating ends at the moment sulphuric acid vapor is given off. But if further heating of the sulphuric acid solution is required to complete the dissolution, the flask with a cork and a reflux condenser must be used since in this case there may be losses in boron through evaporation. The data we obtained on the volatility of boric acid are in agreement with data already published /2/.

Determining the boron

The usual method of determining boron in the filtrate after precipitation of the metal component in the boride with barium carbonate was not applied in this case since the boride had been dissolved in sulphuric acid. Hence we used two versions of the method of determining the boron:

- 1) titration with alkali in the presence of a cation complexed by an organic oxy-acid;

- 2) titration of the boron in the filtrate after precipitation of the cation by an alkali in the form of the hydroxide of the corresponding metal.

As complexing agents for cations of the metals titanium, zirconium and chromium, we tested oxalic, tartaric and citric acids. Comparative tests showed that the best results were obtained when titrating the boron in the presence of tartaric acid, which was used from then on in our analysis.

A clearcut change in the color of the indicator at the point of equivalence is ensured by adding a small excess of mannitol to the solution. The data obtained for the determination of boron in titanium and zirconium borides in the presence of tartaric acid are shown in Table 1.

Table 1

Determining boron in titanium and zirconium borides (titration in presence of tartaric acid and phenolphthalein).

Boron content in specimen, %	Boron found in specimen, %	Relative error, %	Name of specimen
15.08	15.10	+0.13	Titanium boride
15.08	14.84	-1.73	" "
15.08	15.21	+0.86	" "
29.74	29.45	-0.97	Titanium diboride
29.74	29.84	+0.33	" "
29.74	29.74	0	" "
8.25	8.34	+1.09	Titanium boride
8.25	8.20	-0.60	" "
8.25	8.40	-1.81	" "
5.78	5.88	+1.73	" "
5.78	5.76	-0.02	" "
24.72	24.60	-0.49	Titanium diboride

These data suggest that the titration of boron in the presence of a complexing agent is sufficiently accurate and reliable for the metal ion. A shortcoming of the metal is the large consumption of mannitol. In the case of chromium boride, this method could not be used since chromium solutions are strongly colored.

The second method we suggest consists in separating the metals by precipitation by alkalis in the form of hydroxides. The solution plus the hydroxide residue are transferred to a measuring flask, topped up with water and allowed to settle. An aliquot part of the solution is filtered off through a dry filter, acidulated to the extent of a slight acid reaction and the excess acid is titrated with 0.1 m solution of alkali with methyl red as the indicator. Mannitol is then added and the boric acid is titrated in the presence of phenolphthalein.

When analyzing chromium boride the trivalent chromium is precipitated by alkali, the pH value of the solution is strictly ~~maintained~~ (caustic soda is added until the color of the phenolphthalein changes) and the solution is boiled. Boiling the solution promotes hydrolysis of the chromite with the formation of chromium hydroxide

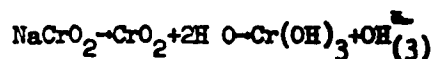


Table 2 shows data for the determination of boron by this method in artificial mixtures of borides and the standard boric acid solution.

Table 2
Determining boron in mixtures of borides and standard boric acid solution
(0.2 g boride).

	Boron contained in weighed boride, mg	Boron added, mg	Boron content with additive, mg	Boron found, mg	Relative error, %
TiB₂	56.0	5.4	61.4	62.0	+0.97
		8.64	64.64	64.3	-0.52
		18.36	74.36	75.0	+0.86
		21.60	77.60	77.7	+0.13
ZrB	13.76	18.36	32.12	31.90	-0.68
		10.80	23.56	24.80	+0.97
		21.60	35.36	35.50	+0.39
		18.36	32.12	32.20	+0.24
Boride chrome	25.50	10.80	36.30	35.90	-1.10
		6.48	31.98	31.10	-2.75
		16.20	41.70	42.10	+0.95
		8.60	34.10	33.60	-1.46

Determining titanium

Titanium obtained by dissolving titanium boride or diboride in a mixture of sulphuric and perhydrol is reduced to the trivalent state with zinc metal in Somey's apparatus (see drawing).

Table 3
Comparative determination of titanium in titanium borides (TiB₂ and TiB).

Titanium content in boride, % (amalgam method)	Titanium obtained, %		Error, %	
	By titrating with ferric-ammonium sulphate	By titrating with potassium bichromate	Absolute	Relative
67.30	67.34	—	0.04	+0.06
67.30	67.18	—	0.12	-0.17
67.30	67.15	—	0.15	-0.22
67.30	—	67.13	0.17	-0.25
67.30	—	67.15	0.15	-0.22
73.55	73.56	—	0.01	+0.01
73.55	73.32	—	0.23	-0.31
73.55	—	73.36	0.19	-0.26
73.55	—	73.54	0.01	-0.01
73.55	—	73.36	0.19	-0.26

The determination is completed by one of two versions of the volumetric method:

a) by direct titration with a solution of ferric-ammonium sulphate in the presence of a rodanide ion as the indicator;

b) titration of bivalent iron ions reduced with Ti^{3+} ions by a solution of potassium bichromate.

Both versions were checked with a standard solution of titanium. Table 3 shows data for comparative determination of titanium in titanium borides.

Determining chromium

A solution of chromium sulphate obtained when chromium boride has been dissolved in a mixture of sulphuric acid in perhydrol was neutralized until the reaction was slightly alkaline, after which the chromium was oxidized with hydrogen peroxide. The excess oxidizing agent was destroyed by boiling the alkaline solution for a few minutes. The chromate solution obtained was acidulated and as soon as phosphoric acid had been added, was titrated with a Mohr's salt solution. The titer for the latter was verified with a potassium bichromate solution especially prepared on the day of the analysis. The titration was carried out in the presence of diphenyl-aminosulphanate of sodium.

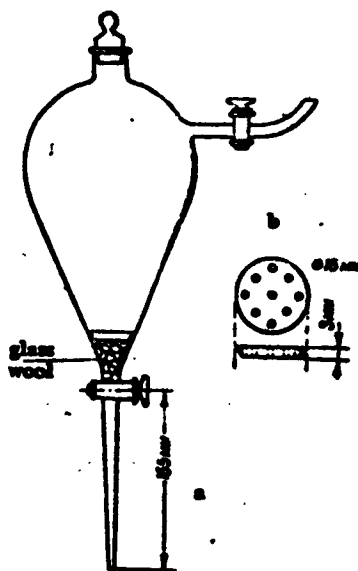


Fig. 1. Sweeney's apparatus
a) general view; b) insert- porous plate

The results of the determination of chromium in chromium borides are shown in Table 4.

Table 4
Comparative determination of chromium in chromium boride.

Chromium content in boride, %		Relative error, %	Chromium content in boride, %		Relative error, %
Determined after boride is melted with soda	Determined after acidic composition		Determined after boride is melted with soda	Determined after acidic composition	
80.64	80.64	0.0	64.32	64.33	+0.02
80.64	80.64	0.0	64.32	64.33	+0.02
80.64	80.64	0.0	64.32	64.54	+0.34
80.64	80.56	-0.09	59.16	59.41	+0.42
81.24	81.47	+0.28	59.30	59.44	+0.23
81.54	81.54	0.0	59.30	59.30	0.0
81.23	81.47	+0.28	59.30	59.30	0.0
81.23	81.46	+0.24	81.24	81.47	+0.24
81.23	81.48	+0.30	81.24	81.54	+0.37

Determining zirconium

The method is based on the reaction between zirconium and versene. The sulphuric acid solution of zirconium obtained when zirconium boride was dissolved in a mixture of sulphuric acid and perhydrol was boiled to change the zirconium ion into a zirconil ion ZrO^{2+} .

The zirconium content in the solution obtained was determined by the reverse titration method, for which excess versene was added to the $ZrOSO_4$ solution. The solution was neutralized with ammonia in the presence of congo red until the pH value was 5. Sulphosalicylic acid was the indicator and the excess versene was titrated with a titrating solution of ferric-ammonium-sulphate.

The results of the complexometric determination of zirconium in zirconium borides and mixtures of zirconium borides with a standard solution of the latter show the fairly high accuracy and reliability of the method (Table 5 and 6).

the solution and titrated with a 0.1 M alkali solution until it turns yellow, after which mannitol is added and the titration is continued with alkali using phenolphthalein as the indicator, and taking this to be the commencement of the boron titration. The titration is completed if the addition of a new portion of mannitol does not remove the pink color of the solution.

Determining boron (version II). The sample is dissolved in the same way as in I. 2 mm 1% solution Mohr's salt and 10 ml 5% solution tartaric acid are added to the sulphuric acid solution obtained and the resulting solution is neutralized with a 20% caustic soda solution. 10 ml 0.1 N sulphuric acid solution is added, the resulting solution transferred to a 200 ml measuring flask and topped up to the mark. An aliquot part of the solution (50 ml) is titrated with a 0.1 N solution of alkali until the phenolphthalein turns it red, after which excess mannitol is added and the titration continued, taking this to be commencement of the boric acid titration.

Determining zirconium. 0.05 g zirconium boride is dissolved by heating in a mixture of 20 ml hydrogen peroxide and 20 ml sulphuric acid (1:4). As soon as SO_3 vapor begins to be given off, the specimen is entirely dissolved; the solution is cooled and carefully topped up with water to 50 ml. 20 ml 0.02 M versene solution is added to it and neutralized with ammonia until the congo paper turns violet, an attempt being made to avoid excess ammonia. The solution is heated up to 70°, 1.5 g sulphosalicylic acid is added and titrated with 0.04 M solution of ferric-ammonium sulphate until it turns from lemon yellow to red yellow. The zirconium is calculated from the equation

$$Z = \frac{N(v_1 - v_2) \cdot T \cdot 100}{a} [\text{wt. \%}]$$

where N is the molarity of the versene solution; v_1 is the volume of the same solution added to the flask prior to titration, ml; v_2 is the volume of the ferric-ammonium sulphate solution, ml; k is the conversion factor (ratio of molarity of ferric-ammonium sulphate solution to molarity of versene); T is the titer of the versene with

respect to zirconium, g/ml; x is the portion of boride in g.

Determining chromium. 0.1 g chromium boride is dissolved by heating in 20 ml of a mixture of hydrogen peroxide and 20 ml sulphuric acid (1:4). The heating is completed in 3 or 5 minutes as soon as SO_3 vapor begins to appear, and the Cr^{3+} ion turns green. The solution is cooled, diluted with water and neutralized with a 20% solution of caustic soda with congo paper as the indicator. We then add 4 ml hydrogen peroxide and boil for 5 to 7 minutes until the chromium is completely oxidized. The yellow chromate solution is neutralized with a sulphuric acid solution (1:4) with the same indicator, this time adding 5 ml excess. The solution is transferred to a 250 ml measuring flask and topped up to the mark with water. To the aliquot part of the solution (50 ml) we add 1 ml orthophosphoric acid and titrate the chromium with a 0.1-n Mohr's salt solution in the presence of sodium diphenyl-aminosulphonate as the indicator. The total amount of solution for the titration should be about 150 ml.

Determining titanium. 0.05 g boride is decomposed by heating in a mixture of 20 ml hydrogen peroxide and 20 ml sulphuric acid (1:4) until sulphuric anhydride vapor appears and the boride is completely dissolved. The liquid is then cooled and cautiously topped up with up to 20 ml water. The solution is transferred qualitatively from the flask into a Somey apparatus, where it is diluted with wash water until the total volume of liquid in the apparatus is 50 ml. Reduction of the titanium by zinc metal in the Somey apparatus lasts 25 minutes.

Just before the reduction is complete, the apparatus is connected to a Kipp's apparatus and a stream of carbon dioxide is passed through. The reduced solution is poured off through the bottom tube in the apparatus into a conical flask containing 40 ml water saturated with carbon dioxide. 10 ml 50% solution ammonium rhodanate is added and the reduced titanium is titrated in a carbon dioxide stream with a 0.05 solution of ferric-ammonium sulphate until it turns red.

Conclusions

1. A method has been developed for acidic decomposition of titanium, chromium and zirconium borides.
2. A method has been developed for volumetric determination of the boron in borides without the usual preseparation of the elements.
3. The possibility has been shown of the volumetric complexometric determination of zirconium in a sulphuric acid solution of zirconium boride.
4. A method has been put forward for non-amalgam reduction of titanium followed by determination of it by the reductometric method.

CHEMICAL PROPERTIES AND ANALYSIS OF SOME NITRIDES

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The nitrides of high-melting metals as well as those of boron and silicon are of great practical importance. For example, titanium, zirconium, niobium, tantalum, vanadium, chromium, silicon and boron nitrides possess high electric resistance and are therefore used in electrical engineering. Furthermore, they are employed to make refractories, high-temperature heating alloys and so on /1/. The adoption of high melting compounds makes it necessary to study their chemical properties thoroughly and to work out rational methods of analyzing them.

In this paper we consider some of the chemical properties and methods for analyzing the following nitrides: BN, Si_3N_4 , TiN, ZrN, NbN, TaN, Cr_2N , CrN, VN, V_2N , AlN, MgN. Except for aluminum and magnesium nitrides, these compounds are fairly stable with respect to a variety of chemical reagents /2-7/. All the nitrides are decomposed when melted with alkalis and sodium hydroxide.

Magnesium and aluminum nitrides are less stable compounds. Magnesium nitride decomposes in air (it is kept in ampoules) and is easily dissolved in acids; aluminum nitride dissolves in diluted alkalis /9/.

Chromium and vanadium form nitrides with the composition V_2N , Cr_2N , VN, CrN. V_2N and Cr_2N dissolve in certain acids and VN and CrN do not, except for nitric and perchloric acids, respectively /2/.

Extremely little data have been published on analysis of pure nitrides of high-melting metals. The published material in effect only concerns analysis of the nitrides which are contained in steels in the form of impurities. But nitrides may behave differently in the free state and under different sets of conditions. Hence, we felt it necessary to study methods of dissolving pure nitrides and working out methods of chemically analyzing them.

It is known [2, 11, 12] that the residues insoluble by the normal method (after dissolution of the steels) contain nitrides. The following methods are suggested for decomposing them;

- 1) conversion into solution by melting with potassium bisulphate in the presence of sulphuric acid;
- 2) melting with sodium peroxide or a mixture of lead chromate and lead oxide; the nitrogen content in the residue is found from the amount of gas given off;
- 3) dissolving in alkali.

The most convenient method of decomposing the sample is one in which the entire weighed portion is dissolved (without separating and further decomposing the insoluble residue).

To find suitable methods of decomposing the nitrides, and also to study the chemical properties, we investigated the solubility of titanium, zirconium, niobium, tantalum, chromium nitrides in different acids, mixtures of acids and alkalies.

The nitrides were prepared at the Institute of Metal Ceramics and Special Alloys by nitriding metals at high temperatures [1]. According to the chemical and x-ray analyses, the composition of the nitrides we studied was close to the theoretical composition.

Our method of investigating the solubility was as follows: a weighed portion of nitride is dissolved in a 100 ml beaker in different media in the cold state for a day and heated for 2 or 3 hours. The insoluble residues are filtered off through a No. 4 glass filter, washed, dried and weighed. The content of the metal and nitrogen in the solution is then determined. The total ($M_{\text{sol}} + N_{\text{sol}} + \text{insoluble residue}$) was always close to 100%.

The results of the study of the solubility of certain nitrides are shown in Table 1.

From the data obtained, it follows that the most stable nitrides in the

group Ti-Zr-Nb-Ta-Cr are tantalum and chromium nitrides (CrN), while the least stable are zirconium nitride and chromium nitride (Cr₂N). Table 2 gives data on the complete solubility of the nitrides.

Table 1
Chemical stability of nitrides in acids and alkaline solutions¹.

Medium	TiN	ZrN	NbN	TaN	CrN	Cr ₂ N
HCl (1:1)	1/2	4/85	1/6	2/1	-/4	-/100
H ₂ SO ₄ (1:4)	2/5	47/55	1/16	0	-/0	-/100
HNO ₃ (1:1)	89/95	4/31	2/0	1/2	-/2	-/2
HClO ₄ (1:3)	2/6	0/2	0/0	0/-	-/-	-/-
HCl, d=1.19	1/2	11/84	0/1	1/2	-/6	-/100
H ₂ SO ₄ , d=1.84	3/76	55/100	0/100	0/23	-/0	-/x
HNO ₃ conc.	90/**	2/36	1/0	2/2	-/8	-/3
HClO ₄	1/**	1/2	2/0	0/2	-/100	-/100
H ₂ O ₂	-/98	-/0	-/84	-/59	-/0	-/2
HCl + HNO ₃ (3:1)	87/-	18/75	1/1	-/0	-/9	-/2
HClO ₄ + HCl (1:1)	2/-	24/88	2/5	-	-/5	-
HNO ₃ + H ₂ O ₂ (1:1)	98/97	6/35	74/85	-	-/2	-/0
HNO ₃ + HF	-/100	-/100	-/100	-/100	-	-
H ₂ CO ₃ + H ₂ SO ₄ (3:1)	2/24	10/-	-/-	-	-	-
H ₂ SO ₄ + H ₂ O ₂ (2:1)	97/99	75/-	-	-/7	-/2	-/3
H ₂ SO ₄ + HNO ₃ + H ₂ O ₂ (1:1:4)	59/98	19/-	-	-	-	-
K ₂ SO ₄ + H ₂ SO ₄ (10g + 10ml)	-/100	-/100	-/100	-/100	x	x
NaOH - 1% solution	-/*	-/0	-/4	-/7	0	0
NaOH - 10% solution	-/*	-/0	-/13	-/*	0	0
NaOH - 40% solution	-/*	-/58	-/19	-/*	0	0
1% NaOH + H ₂ O ₂	-/91	-/1	-/83	-/16	-	-
10% NaOH + H ₂ O ₂	-/84	-/13	-/100	-/61	-	-
40% NaOH + H ₂ O ₂	-/57	-/52	-/100	-/**	-	-

Note. *—Partial dissolution with hydrolysis; **—Solution of most of the nitride accompanied by hydrolysis; x—formation of basic salts.

¹ The figures show the percentage of solution in the cold state (numerator) and when heated (denominator).

Table 2

Ni- tride	Total solubility of nitrides.					
	Solvent					
TiN	HNO ₃ + HF	H ₂ SO ₄ + K ₂ SO ₄	HNO ₃ + HCl (1:3)	H ₂ O ₂		
ZrN	Ditto	Ditto		H ₂ SO ₄ (sp. gr. 1.84)		
NbN	Ditto	Ditto		Ditto	H ₂ O ₂ + NaOH	
TaN	Ditto	Ditto				
Cr ₂ N					HClO ₄	HCl (1:1) + HCl (sp. gr. 1.19) + H ₂ SO ₄ (1:4)
CrN					Ditto	

Determining nitrogen in nitrides

Two basic methods have been published for determining nitrogen: the Dumas method, which involves burning the nitride with an oxidizing flux and recording the molecular nitrogen, and the Kjeldahl method by which the nitrogen is distilled in the form of ammonia. It should be mentioned that to determine the nitrogen in nitrides, particularly in titanium and zirconium nitrides, the Dumas method is the one usually used. But it is a complex and long drawn out operation and unsuitable for mass analysis. In accuracy of determination it is not superior to the distillation method. Clearly, the distillation method has rarely been used for analyzing nitrides since the solubility of the latter has not been adequately studied.

Table 3

Comparative data on determining nitrogen in chromium nitrides
by the Dumas and Kjeldahl methods.

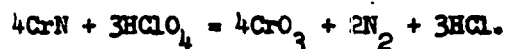
Specimen	Nitrogen obtained, %		
	By distillation after dissolving in perchloric acid	By the Dumas method	By distillation after dissolving in sulphuric acid (1:4)
CrN	1.3	20.4	—
Ditto	0.7	21.0	—
Cr ₂ N	0.4	—	11.8
Ditto	0.2	—	10.9
CrN+Cr ₂ N	2.3	17.5	—
Ditto	0.2	15.6	—

In our laboratory practice nitrogen in most nitrides is determined by distillation. The results obtained by this method agree with the results obtained by Dumas' method.

In dissolving the nitrides we made use of both our own as well as published data on solubility. The nitrides were dissolved in the following acids or alkalies: ZrN, NbN in concentrated sulphuric; TiN, TaN, BN, VN in a mixture of sulphuric acid and potassium sulphate; Cr₂N, MgN in sulphuric acid (1:4); AlN in a 40% alkali solution.

Chromium nitride CrN is only soluble in perchloric acid /7, 11/. Our data show that when chromium nitrides (both CrN and Cr₂N) are dissolved in perchloric acid and the nitrogen is then determined by distillation, we observe almost complete loss of the nitrogen (Table 3).

Clearly, when chromium nitrides are dissolved in perchloric acid, free nitrogen is generated as follows



Consequently, Kjeldahl's method is not suitable for analyzing chromium nitride CrN.

Silicon nitride is insoluble in acid /7/. Thus, in the nitrides CrN and Si₃N₄ the nitrogen was determined by the Dumas method. As the flux we used a mixture of lead oxide and lead chromate in the proportion of 1:1.

Determining metal in nitrides

Titanium, zirconium, niobium and tantalum nitrides. To determine the metal, niobium and zirconium nitrides were dissolved in concentrated sulphuric acid with heating, while titanium, tantalum nitrides were dissolved in the mixture of hydrofluoric and nitric acids, and in aqua regia. The metal was then precipitated out with cupferron or else determined by the volumetric method (titanium).

High speed methods are very important for mass analyses. We know from published literature /13/ that titanium, zirconium, niobium and tantalum nitrides change to oxide at high temperatures. We took advantage of this fact in determining the metal in the nitrides of titanium, zirconium, niobium and tantalum. The results obtained by the high-speed method agreed closely with results obtained by the ordinary method (Table 4).

The magnesium in magnesium nitride was determined by complexometric titration after the compound had been dissolved in hydrochloric acid (1:1) /14/.

The vanadium in vanadium nitride was determined by the volumetric method after the sample had been dissolved in nitric acid /12/.

Table 4
Comparison of methods of determining
metals (calcining and precipitation) in
nitrides.

Nitride	Metal obtained, %	
	By calcining	By precipitation
TiN	77.0	77.0
Ditto	76.9	77.0
ZrN	89.4	89.3
Ditto	89.2	89.3
NbN	86.5	86.7
Ditto	87.1	87.0
TaN	92.6	92.8
Ditto	92.9	92.9

Chromium nitride (Cr_2N) was dissolved in sulphuric acid (1:4). The chromium was determined by the persulphate-silver method /12/.

The chromium nitride (CrN) is insoluble in acids, except for perchloric acid, though the latter cannot be used on account of evaporation of the chromium. The sample of chromium nitride was therefore melted together with sodium peroxide in a nickel or iron crucible, after which the chromium was determined by the volumetric method /12/.

Separation of the nitrides CrN and Cr_2N . It often happens when preparing chromium nitride CrN that we obtain a mixture of nitrides $\text{CrN} + \text{Cr}_2\text{N}$. The pure nitride CrN can be separated from this mixture on the basis of solubility data. With this aim, 0.4 g of the compound is heated in sulphuric acid (1:4) until it dissolves, the insoluble residue is filtered off through a No. 4 glass filter, washed with water and dried. Here the CrN goes into the solution; the pure nitride Cr_2N is left in the insoluble residue. The filtrate and the residue can be analyzed for chromium and nitrogen content in the way described above.

Determining boron in boron nitride

A weighed sample of boron nitride is melted together with soda in a platinum crucible. The melt is leached with hydrochloric acid (1:1) and the boron is then determined by the volumetric method /8/.

Determining total silicon content in silicon nitride

The weighed sample is melted together with sodium peroxide in an iron crucible. After precipitation the melt is leached with water and the determination is then conducted by the hydrochloric acid method /12/.

The method of determining free silicon in silicon nitride is based on the solubility of free silicon in a 1% caustic soda solution. Here the silicon nitride does not dissolve. The silicon content in the solution obtained is determined colorimetrically from the yellow coloring of the silicon-molybdenum acid /12/.

Conclusions

1. We studied the solubility of titanium, zirconium, niobium, tantalum and chromium nitrides in different acids, mixtures of acids, and alkali solutions.
2. It was shown that tantalum nitride and chromium nitride (CrN) are the most resistant to the action of different solvents, while zirconium nitride and the chromium nitride Cr_2N are the least stable.
3. The results of our study of solubility of nitrides are applicable to decomposition of specimens during analysis; methods of analyzing certain nitrides are given.

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CHEMICAL PROPERTIES AND METHODS OF ANALYZING CERTAIN

SILICIDES

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The silicides of high-melting metals in the fourth, fifth and sixth groups of the periodic table are distinguished, apart from high resistance to oxidation in the air and to different acids and acid mixtures, by comparatively high-melting points, hardness, semiconductor characteristics and a number of other technically important properties, on account of which they are widely employed in engineering /1, 2/, particularly as heat-resistant alloys, high-temperature resistance furnace heaters, radio engineering and electronics.

Published literature contains descriptions of the chemical properties of these silicides, but methods of chemically analyzing them have hardly been developed at all.

Disen and Huttig /3/ give data on the behavior of silicides of the transition metals in certain media, which show that the mineral acids, except for hydrofluoric acid and mixtures of it with other acids, do not decompose them.

This paper studies the behavior of silicides in a number of media with a view to establishing rational methods of chemically analyzing them.

The disilicides used for our study were obtained by synthesis from elements by a group of staff members at the Institute of Metal Ceramics and Special Alloys under the guidance of G. V. Samsonov /4/. Data on the composition of the silicides used are given in Table 1.

The disilicides obtained were pulverized and passed through a 270 mesh screen. In all the experiments samples of silicide weighing 0.1 - 0.2 g were treated with 40 ml of the corresponding acid or acid mixture and heated to 100 - 120° for two

hours. The insoluble residue was filtered off, dried and weighed. The content of metal which had passed into the solution was determined in the filtrate. Data on the chemical stability of the silicides in different media are shown in Table 2.

Composition of disilicides used.

Table 1

Silicide	Metal content, %		Silicon content, %			
	Theoretical	Experimental	Theoretical	Experimental		
				Si _{ov}	Si _f	Si _b ¹
TiSi ₂	46.20	45.50	53.80	54.0	0.32	53.85
VSi ₂	47.66	46.90	52.34	52.37	0.29	52.23
TaSi ₂	73.37	76.12	23.69	22.51	0.34	22.24
GrSi ₂	48.15	48.08	51.85	49.93	0.73	49.56
MoSi ₂	63.10	64.57	36.90	34.72	0.12	34.61

Our data suggest that all the disilicides dissolve quickly and completely in mixtures of nitric and hydrofluoric as well as sulphuric and phosphoric acids. However, these mixtures cannot be recommended for dissolving the silicides and making a solution for determining the overall silicon. If use is made of the mixture HF+HNO₃ the silicon evaporates in the form of SiF₄, but if H₂SO₄+H₃PO₄ is used the silicic acid dissolves with the formation of (SiO)(PO₃)₂ /5/, hence the only method of transferring the silicides to the solution in this case is to melt them together with soda, caustic soda or sodium hydroxide. Melting them with sodium carbonate requires the use of a platinum vessel and is therefore inconvenient. Melting them with sodium hydroxide which is conducted in iron or nickel crucibles, gives good results. Here it must be kept in mind that the use of a large excess of sodium hydroxide (more than 10 x the amount of the sample) leads to considerable losses through the vigorous decomposition of the peroxide itself.

The best method of transferring most silicides into the solution is to melt them with caustic soda in a nickel crucible. Here the amount of nickel passing into the solution is, for practical purposes, negligible.

In chemical analysis of the silicides, we determine the overall content of

silicon, free silicon and metal.

Table 3

Disilicide	HCl (a. g. b. 1.19)		HF + HNO ₃		HCl + HNO ₃ (3:1)	
	Insoluble residue, %	Metal content in solution, %	Insoluble residue, %	Metal content in solution, %	Insoluble residue, %	Metal content in solution, %
TiSi ₂ (ZrSi ₂)	—	—	0	—	95.5	2.0
VSi ₂	—	—	—	—	—	—
TaSi ₂ (NbSi ₂)	—	—	0.2	—	95.5	0.7
CrSi ₂	44.5	26.0	0	—	91.6	3.5
MoSi ₂	99.8	Not detected	0	—	99.0	traces
WSi ₂	—	—	—	—	—	—

Insoluble residue, %	Metal content in solution, %	Insoluble residue, %	Metal content in solution, %	Insoluble residue, %	Metal content in solution, %	Metal content in solution, %
0	—	86.4	8.1	85.5	8.8	Not detected
—	—	—	—	—	—	Ditto
0	—	96.5	3.0	96.6	2.6	"
0	—	41.4	26.0	62.8	—	"
0	—	99.2	Not detected	—	—	"
—	—	93.4	—	—	—	"

Determining overall silicon content in silicides

As has already been pointed out, to transfer the silicides to the solution when determining the overall content of silicon, it is best to melt them with caustic soda in nickel (or iron) crucibles. The melt should be leached in an approximately 10% solution of sulphuric or hydrochloric acid.

Further determination of the silicon in chromium, vanadium, molybdenum, thorium, manganese, iron, nickel or cobalt silicide presents no difficulty and can be conducted by either the sulphuric-acid or hydrochloric-acid method.

Most interesting of all is the determination of the total amount of silicon in silicides of titanium, zirconium, niobium, tantalum and tungsten. The use of the

sulphuric and hydrochloric acid method of producing silicic acid leads in this case to precipitation of a considerable amount of metal together with SiO_2 in the form of the metal oxides, thus hampering further determination of the SiO_2 content.

In order to prevent this happening, for the silicides of these metals we used the method of adding a complexing agent to the solution in the form of an easily soluble compound to retain the metal. A similar method has been put forward by Pen'kova and Yakovlev /6/ for determining the silicon in niobium alloys.

To determine the overall content of silicon in titanium silicide, we used the perchloric acid method of producing silicic acid. In this case TiO_2 is not precipitated together with SiO_2 . It should be pointed out that the precipitated residue of silicic acid must be thoroughly washed with water until all the perchloric acid is removed.

Table 3
Silicon content in TiSi_2 determined by sulphuric acid and perchloric acid methods.

No. of sample	Si content, %		Relative deviation, %	
	Sulphuric acid method	Perchloric acid method	Sulphuric acid method	Perchloric acid method
1	52.90; 49.97; 63.60	51.10; 51.04	5.5	0.11
2	55.06; 56.71	57.76; 57.73	1.8	0.40
3	50.86; 52.60	54.69; 54.57	3.3	0.20

Table 3 shows data obtained for SiO_2 in titanium silicides by the sulphuric acid and perchloric acid methods.

To determine the silicon in niobium silicide (NbSi_2), tantalum silicide (TaSi_2) and tungsten silicide (WSi_2) we added a saturated solution of oxalic acid to our solution after the sulphuric acid solutions had been evaporated until SO_3 appeared. This prevented hydrolysis of the niobium, tantalum, and tungsten, and the silicic acid is not contaminated by the oxides.

The method was checked with TaSi_2 specimens and an artificial mixture WO_3 - SiO_2 by the additive method.

The data obtained is shown in Table 4.

Consequently, the precipitation of silicic acid in the presence of oxalic acid is quite suitable for determining the overall silicon content in niobium, tantalum and tungsten silicides.

Table 4
Results of determining silicon content in TaSi₂ and artificial mixture WO₃·SiO₂.

No. of sample	TaSi ₂			No. of sample	WO ₃ ·SiO ₂		
	Si added, g	Si found, g	Relative error, %		SiO ₂ added, g	SiO ₂ found, g	Relative error, %
1	0.0456	0.0465	2.0	1	0.0491	0.0501	2.0
2	0.0380	0.0376	1.0	2	0.0596	0.0573	3.9
3	0.0420	0.0426	1.4	3	0.0548	0.0551	1.5
4	0.0388	0.0384	1.0	4	0.0484	0.0496	2.4
				5	0.0508	0.0517	1.7
Mean error			1.3				2.3

Our experiments show that when determining the overall silicon content in zirconium silicides (ZrSi₂), citric acid should be added as the complexing agent. The addition of oxalic acid does not produce the desired result. It should be pointed out that when analyzing zirconium silicide, when the silicic acid has been precipitated in the presence of citric acid, the filtrate cannot be used to determine the zirconium present by any of the known methods (cupferron, phosphoric acid methods). A considerable amount of zirconium is left in the solution in this case.

Determining free silicon

The determination of free silicon in silicides is based on dissolving the free silicon in a 1% solution of caustic soda followed by calorimetric determination of the silicic acid formed in the form of a yellow silicic-molybdic heteropoly acid.

In order to establish whether or not it is possible to use the given method for determining the free silicon in the silicides, we must first ascertain the stability of the silicides in a 1% solution of alkali. The experiments conducted for this purpose were as follows. A weighed portion of the silicide in question (0.5 - 1.0 g) was heated and treated with 1% alkali solution in a platinum bowl for 40, 60 and 90 minutes. The insoluble residue was filtered off and the silicon content in the fil-

trate was determined. If the silicon content in the solution was constant, no matter how long the solution was boiled, it can be assumed that the silicide does not dissolve in a 1% caustic soda solution.

The second method we used to check the stability of silicides in a 1% alkali solution was to treat 1.5 - 3 g disilicide with a 1% caustic soda solution for a set period of time. The insoluble residue was filtered off and carefully washed. The silicon content in the filtrate was then determined. The filtrate plus the residue were dried, and a sample of the dry residue was taken for a second determination of the free silicon. Sometimes the operation was carried out a third time. We were thereby able to establish that the free silicon can be determined in this way in the disilicides of titanium, zirconium, tantalum, chromium, vanadium, molybdenum, thorium, iron and manganese. The silicides of niobium, tungsten, cobalt and nickel dissolve in a 1% solution of caustic soda, and we cannot therefore recommend determining the free silicon in these silicides by treatment with this solution.

On the basis of data we suggest the following method for determining the free silicon in disilicides of titanium, zirconium, tantalum, chromium, vanadium, molybdenum, thorium, iron and manganese: 0.2 - 0.5 g samples of silicide are treated with 40 ml 1% caustic soda solution in a platinum bowl with heating for 45 to 60 minutes. The insoluble residue is filtered off and the free silicon content is determined in the filtrate calorimetrically by measuring the optical density of the yellow silicic-molybdic complex solution. The free silicon content is found from a calibration curve. The latter is plotted for a standard specimen of sodium silicate prepared by dissolving silicon in a 1% caustic soda solution.

Determining metal in silicides

The amount of metal in silicides can be determined by two methods: 1) in the filtrate after separating the silicic acid, or 2) in the solution after removing the silicon in the form of SiF_4 by treating the silicide sample with a mixture of

hydrofluoric and nitric acids in a platinum bowl.

In most cases the second method is preferred, since it excludes errors due to metal impurities in the iron and nickel crucibles.

The metal in the solution is determined by one of the accepted analytical methods /7, 8/, for example, vanadium is determined in a sulphuric acid solution, manganese is determined by the volumetric method, niobium and tantalum by precipitation with cupferron, cobalt is precipitated from a hydrochloric acid solution with α -nitroso- β -naphthol, and so on.

We developed a high-speed method for determining cobalt. The method is based on the fact that after the silicide sample has been dissolved in a weighed bowl, in a mixture of hydrofluoric and nitric acids to which sulphuric acid is further added, the silicon evaporates in the form of SiF_4 , and as soon as the sulphuric acid residues have been removed by heating in a muffle furnace at $450 - 475^\circ$, CoSO_4 is left in the platinum bowl and then weighed.

Conclusions

1. We studied the behavior of the disilicides of transition metals in the fourth, fifth and sixth groups of the periodic table in a number of acidic and alkaline media. It was found that the silicides are completely decomposed in a mixture of hydrofluoric and nitric acid as well as phosphoric and sulphuric acids.

2. The most effective way to transfer the silicides to a solution when determining the overall silicon content in them is to melt them with caustic soda in nickel or iron crucibles. We developed methods for determining the overall silicon content in the silicides of tungsten, niobium, tantalum, zirconium, based on bonding of the metal into a soluble complex compound with oxalic acid (W, Nb, Ta) or citric (Zr) acid with the precipitation of SiO_2 . The silicon in titanium silicides can be determined by the perchloric acid method.

3. We developed a method of determining free silicon in the disilicides

of titanium, zirconium, tantalum, thorium, chromium, vanadium, molybdenum, iron and manganese, based on dissolving the free silicon in a 1% caustic soda solution.

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